

**DEVELOPMENTS IN AMTEC DEVICES, COMPONENTS AND PERFORMANCE**

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CAMERA READY MANUSCRIPT prepared for

Eleventh Symposium  
on Space Nuclear Power and Propulsion  
Albuquerque, INew Mexico  
9-13 January 1994

initial submission: Sept. **20, 1993**

final submission:

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### Abstract

Improvement of the performance of an AMTEC device requires improvement and development of components as well as of device geometry and construction. The research and development effort at JPL includes studies which address both overall device construction and studies of components. This paper discusses recent studies on components and devices which have been carried out at JPL. Components investigated include the electrode materials titanium nitride (TiN) and rhodium-tungsten (RhW) and the electrolyte materials sodium  $\beta$ "-alumina and potassium  $\beta$ "-alumina. We have studied the mechanical characteristics of sodium and potassium  $\beta$ "-alumina ceramic and conditions for fabrication of potassium  $\beta$ "-alumina. Device studies include fabrication and operation of a wick fed cell using a graded, sintered wick, a higher voltage vapor-vapor multicell which includes three "subcells" which are internally series connected, and an AMTEC which uses potassium as the working fluid.

### INTRODUCTION

The Alkali Metal Thermal to Electric Converter (AMTEC) is a direct energy conversion device capable of near-Carnot efficiencies. The device is an alkali metal concentration cell which uses a  $\beta$ "-alumina solid electrolyte (BASE) tube as a separator between a high pressure region containing alkali metal at 900 - 1300 K and a low pressure region containing a condenser at 400-700 K. Alkali metal is oxidized at the high pressure metal/BASE interface and metal ions are conducted through the BASE to the low pressure side of the BASE. Electrons travel through an external load to recombine with the ions at a thin film, porous metal electrode (the cathode) which is sputtered onto the outside wall of the BASE tube; alkali metal vapor leaves the electrode and is collected on the condenser (Weber 1974 and Cole 1983). When operated at temperatures of 1100-1150 K, a single AMTEC cell develops an open circuit potential of -1.5 Volts, and typically is operated -0.5 Volts. In some geometries, a metal anode is deposited on the high pressure side of the BASE; in other geometries, liquid alkali metal in contact with the BASE serves as the anode.

The research and development effort in AMTEC at JPL consists of several parallel projects, including both component work and device work. Component work has included electrode materials,  $\beta$ "-alumina solid electrolyte (BASE) studies including potassium- $\beta$ " alumina, and the current collection network. In electrode materials, the comparative performance characteristics of different TiN formulations have been investigated, and the conditions for photodeposition of rhodium-tungsten alloys have been established. In the area of BASE, the fabrication and physical characteristics of potassium-BASE have been investigated and an improved means of making K-BASE ceramic by ion exchange with Na-BASE has been established. The mechanical characteristics of such electrolyte are superior to those of the starting material. Device work includes new cell geometries and set-ups, such as wick-fed cells and the S-Volt vapor-vapor cell, as well as improvements on already existing cell geometries, such as improved heat shields. Three new cells have been operated at JPL, a potassium AMTEC, a wick fed cell using a graded, sintered wick to deliver sodium to the high pressure side of an AMTEC cell, and a series connected 5 Volt vapor-vapor cell. All three show promise for use in particular applications. Potassium AMTECs can be operated at lower temperatures than sodium AMTECs, a graded wick shows promise for high temperature (> 1200 K) wicking, and a cell which has an output of five volts reduces the requirements for power conditioning equipment.

## COMPONENT STUDIES

### Electrode Materials and Current Collection Networks

#### Titanium Nitride

Titanium nitride electrodes have been extensively tested in AMTEC cells, and have shown relatively high power densities and performance (Asakami et al. 1990 and Sievers et al. 1993). A particular advantage of TiN electrodes has been presumed to be its stability against grain growth and material migration, and therefore its potential for use in long-lived devices. Two different types of TiN electrodes were tested together in a Vapor Exposure Test Cell (VETC) so their performance and grain growth characteristics could be directly compared. The VETC is a non-power producing testing apparatus which operates electrode materials as two electrode cells in alkali metal atmosphere. Electrodes are deposited on BASE and contacted as they would be in an AMTEC cell, but are operated potentiostatically as electrochemical cells. It is a relatively simple setup which allows electrode testing without mounting an entire AMTEC experiment (Ryan et al. 1993). One type of TiN was sputter deposited at JPL, by magnetron sputtering titanium in a nitrogen atmosphere. The other type was donated by AMPS, inc. for testing and was deposited by sputtering. Both were contacted with platinum coated molybdenum screens. As shown in the voltammograms in Figure 1, the performance of the two types of TiN was equivalent in the VETC, both in the kinetic region (-0.3 to 0.3 Volts) and in the transport region (where the potential difference between electrodes is greater than 1 Volt). After some time at  $T > 1135$  K the performance of both types declined dramatically. The presence of a surface layer on the electrodes is evident in the later (380 hours) voltammogram, as shown by the hysteresis and apparent reduction wave around +1.0 Volts in the curves in Figure 1.

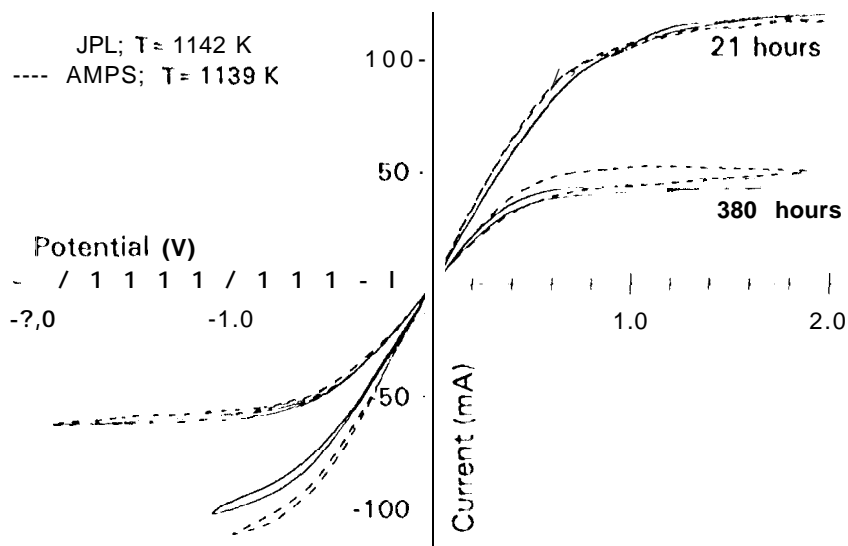


FIGURE 1. Current-Voltage Curves of TiN Electrodes in a Sodium Exposure Test Cell.

In addition, Figure 1 shows the decrease in the current level after several hundred hours of operation. It has been previously shown that TiN will react in the presence of small quantities of oxygen to form  $\text{TiO}_2$  or  $\text{TiO}$ .  $\text{TiO}_2$  is electrically insulating, and it may be the formation of titanium oxides which is responsible for the decline in performance. Long term AMTEC experiments using TiN electrodes have not shown similar decline in performance (Sievers et al. 1993). Those electrodes were contacted with copper wire, which may account for the difference in behavior.

## Rhodium-Tungsten

Rhodium-tungsten electrodes have been used in AMTEC cells and have been among the best performing electrodes (Williams et al, 1989). Because photolytic chemical vapor deposition (PCVD) has been used successfully in fabricating current collection networks (Ryan et al. 1991), this approach to depositing rhodium and rhodium-tungsten has been pursued, with the intention of using PCVD to make integral electrodes and current collection networks.

Rhodium metal was deposited on BASF tube sections by irradiating the BASF in the presence of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  vapor with 248 nm light from a KrF excimer laser. The  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  vapor was introduced into an evacuated chamber by heating a connected chamber containing the solid to  $\sim 310$  K; the  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  sublimates and was carried into the deposition chamber with helium. The entire deposition set-up and technique has been described in detail elsewhere (Ryan et al. 1991).  $\text{W}(\text{CO})_6$  vapor was similarly introduced to the deposition chamber. The pressure in the chamber, including carrier gas and helium buffer gas was  $\sim 200$  Pa (1.5 torr). Rh-W alloys could be formed in the range  $\text{Rh}_3\text{W}$  to  $\text{RhW}_8$  by varying the temperature of the organometallic precursors ( $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and  $\text{W}(\text{CO})_6$ ) and the flow rate of the respective carrier gases. It was also found that higher rhodium content requires that a thin layer ( $< 10$  nm) of rhodium be deposited on the substrate before introducing the tungsten precursor into the deposition chamber. Apparently, rhodium deposition will not compete successfully with tungsten deposition if there is not a rhodium surface available for new rhodium atoms to bond to. In spite of the preference for rhodium to bond to other rhodium deposits, the metals were mixed on the surface, as verified by scanning electron microscopy.

## Electrolyte Studies

Electrolyte studies at JPL have included tests of the mechanical strength of sodium  $\beta''$ -alumina (NaBASF) before and after operation in an AMTEC cell as well as development of techniques for fabrication of potassium  $\beta''$ -alumina solid electrolyte (KBASF) by ion exchange with NaBASF.

Use of potassium as the working fluid in an AMTEC device has a significant advantage over sodium, the fluid used in AMTECs currently being operated and developed. The advantage of potassium is that its vapor pressure is significantly greater than that of sodium at temperatures below 1150 K (Foust 1972), and so a potassium based AMTEC could be operated at lower temperature than a sodium based device. If a potassium  $\beta''$ -alumina solid electrolyte (K-BASF) can be fabricated with conductivity close to that of the sodium electrolyte (Na-BASF), power densities of AMTEC devices in the 800-1150 K operating range should 2-4 times those of the sodium based device, with the greatest improvements in the lower temperature regime. The use of potassium as a working fluid in an AMTEC also allows lower heat rejection temperatures to be more effectively utilized. The higher vapor pressure of potassium effectively reduces transport controlled pressure gradients to a smaller fraction of the "hot side" vapor pressure, and therefore a less significant loss in the AMTEC device performance.

KBASF is an excellent room temperature solid ionic conductor in single crystal forms; its conductivity is greater than that of NaBASF (Briant and Farrington 1980). Fairly dense KBASF ceramics have been prepared by Crosbie and Tennenhouse by ion exchange of Na in NaBASF for K, in KCl vapor at 1300-1400 K (Crosbie and Tennenhouse 1982). A modification of the method used by Crosbie and Tennenhouse was developed to prepare KBASF ceramic tubes from NaBASF ceramic tubes. In this approach,  $\text{K}_2\text{O}$ -rich KBASF powder was first made using a low temperature, sol-gel technique where KBASF is made from alkoxide precursors and fired at as low a temperature as is practical. The NaBASF tube to be exchanged is then buried in the KBASF powder and a KCl exchange carried out at temperatures  $> 1570$  K. The resulting KBASF ceramic has an ionic conductivity about 40% greater than that of KBASF ceramic made using only KCl ion exchange, and small samples were 20-40% stronger than the starting material, as measured by strength tests. Full tubes had strength approximately equivalent to that of the NaBASF starting material.

The increase in mechanical strength of some ion-exchanged KBASF samples led to tests of mechanical strength of NaBASF before and after annealing at 1300 K. Although preliminary results indicated that there may be an increase in strength after annealing or after AMTEC operation, further testing has not shown either increase or decrease in mechanical strength. A recent study by Steinbrück has shown that

there is neither decrease nor increase in bending strength of NaBASE after AMTEC operation (Steinbrück et al. 1993).

## DEVICE STUDIES

Three new devices have been run recently at JPL. These three devices are a potassium AMTEC, a vapor-fed sodium AMTEC which uses a graded wick for sodium return, and a series connected vapor-vapor cell.

### Potassium AMTEC

A NaBASE tube as used for sodium AMTEC cells was ion exchanged as described above to make a KBASE tube. The tube was then brazed to a niobium cup using TiCuNi brazing compound. The Nb cup was brazed to a stainless steel flange, using the same techniques used for NaBASE tubes. A molybdenum film  $\sim 1 \mu\text{m}$  thick was sputter deposited on the outside of the tube to make a  $\sim 0.01 \text{ m}^2$  ( $100 \text{ cm}^2$ ) electrode. The electrode was contacted with molybdenum screen and the tube was mounted in an AMTEC cell; these procedures have been previously described in detail for a liquid-fed sodium AMTEC (Williams et al. 1989). The tube was heated to  $\sim 750 \text{ K}$  and the liquid potassium let into the interior of the cell. The top of the tube cracked because of thermal shock during filling, but the cell operated for a short time with an open circuit voltage of  $0.6 \text{ V}$ , and short circuit current of  $2.5 \text{ A}$ , and a maximum power of  $\sim 0.3 \text{ W}$  ( $\sim 1\%$  total efficiency). Although the failure of the cell so early in life was disappointing, the fact that the cell operated at a measurable efficiency at a relatively low temperature is very encouraging. Projected efficiency at a higher temperature, for example  $1000 \text{ K}$ , would be  $> 15\%$ .

### Wick Fed Cell

A graded sintered wick was constructed to demonstrate the operability of such a wick design. Although mesh and felt type wicks have been previously studied, a sintered wick was selected here owing to its expected potential for smaller pore size and ease of sealing. The theory of wick use and construction has been discussed by several authors (Tanaka 1993, Hunt et al. 1993, Izenson et al. 1993, and Anderson et al. 1993). The graded wick constructed at JPL was made from a stack of 20 sintered stainless steel discs, ranging in pore size from  $20 \mu\text{m}$  to  $0.5 \mu\text{m}$  diameter. The exterior of the stack was plated with brazing alloy mixed with iron powder to prevent vacuum and liquid metal leaks. Higher temperatures require smaller pore sizes to wick liquid metal against the vapor pressure of the high temperature liquid. At  $1100 \text{ K}$ , the optimum pore size for wicking sodium is  $\sim 4 \mu\text{m}$ . A wick with  $0.5 \mu\text{m}$  holes at the high temperature end was constructed to demonstrate the feasibility of higher temperature operation; calculations show that this wick is capable of operation to temperatures greater than  $1200 \text{ K}$  (Tanaka et al. 1993). In addition to capillary force, the issues of alkali metal attack on the wick material at high temperature and of sintering in the wick material must be considered. This stainless steel material will probably be attacked by alkali metal at high temperature, but the sintering decreases the possibility of pores closing because of further sintering. An AMTEC cell using a full tube with a Pt-W electrode was operated for several weeks at  $650\text{--}750 \text{ K}$ . Power was produced and the wick operated well, but at these temperatures there was no demand for a high flow rate.

### Series Connected Multicell

A disadvantage of single AMTEC cells is that they are low voltage, high current devices. A typical AMTEC cell producing  $1 \text{ S W}$  operates at  $0.5 \text{ V}$  and  $30 \text{ A}$ ; the open circuit voltage of such a cell is  $\sim 1.5 \text{ V}$ . This low voltage requires extensive power conditioning to bring the power output to a useable voltage; however, internal series connection of several cells would increase the total output voltage without significantly affecting the power. The multicell demonstrated at JPL consists of several BASE tube sections which are connected to form a single tube; this concept and others have been described in detail (Underwood et al. 1992 and 1993). The individual BASE sections are used to make "subcells" with an anode on the inside of the cell and a cathode on the outside of the cell. Sodium is delivered to the anodes as vapor; the sodium is oxidized as usual and sodium ions are conducted through the BASE while electrons travel through an external circuit. Electrons and sodium ions recombine at the cathode, on the exterior of the tube. The subcells are internally series connected with the anode of one cell

connected to the cathode of the next. A multicell with three subcells would have an open circuit voltage of  $\sim 4.5$  Volts and an operating voltage of  $\sim 1.5$  volts. There is no theoretical limit to the number of cells which can be connected.

As a proof of concept demonstration, a multicell containing, three subcells connected in series was constructed by brazing three BASE sections together, as shown in Figure 2. The sections were brazed to niobium cups using TiCuNi brazing compound. The final open tube section was brazed to a stainless steel flange for mounting in the test cell. Anodes were deposited on the inside of the multicell by painting a dispersion of molybdenum powder and sodium molybdate in brazing cement on the appropriate sections of the multicell and firing at 1200 K to (decompose the brazing cement and anneal the electrode. The electrodes were painted so that they overlapped the niobium cups to provide the series connection to the cathodes, which also overlapped the niobium cups. No further contact was made to the anodes. Cathodes were further contacted by tied on molybdenum screens. The anode lead was the case, as the final anode was contacted to the flange (see Figure 2).

In the experimental vapor-vapor cell assembly, heat is provided by three independent heaters in heater wells above a sodium boiler. The heaters may be moved to ensure that the AMTEC cells are hotter than the boiler. This vapor-vapor cell assembly has been constructed at JPL, as has a multicell with three subcells. The experiment is ready to be mounted and run.

## CONCLUSION

Recent work on AMTEC development at JPL has continued to focus on developing understanding of the operating parameters of components as well as of devices. Work continues on developing electrode materials as well as on understanding the effects of operation on the solid electrolyte. TiN is being tested in a long-term testing cell, and RhW alloys have been made via photolytic chemical vapor deposition. High quality KBASE has been fabricated by ion exchange with NaBASE, and the first AMTEC using potassium as the operating fluid has been run. Current thinking in the AMTEC research community has steered away from the use of electromagnetic pumps for sodium recirculation, and various wick configurations have been proposed. A stacked, sintered wick has been used to recirculate sodium at JPL. Finally, a series connected multicell has been fabricated at JPL, and will be operated to demonstrate the feasibility of making higher voltage devices by series connection into a single tube.

## Acknowledgments

The research described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. It was supported by the NASA, the Department of Energy/Knolls Atomic Power Laboratory, the Air Force Phillips Laboratory, and the JPL Director's Discretionary Fund.

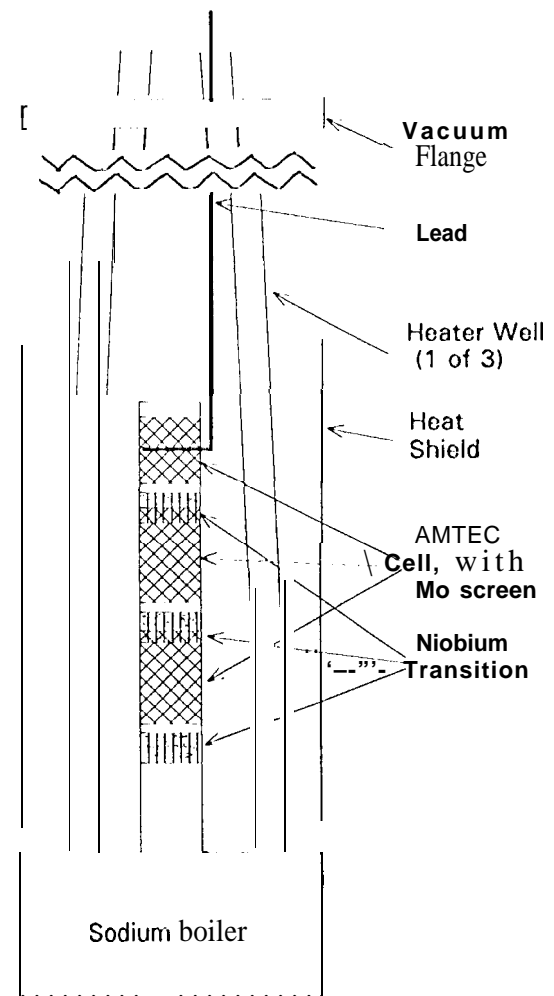


FIGURE 2. Series Connected AMTEC Multicell.

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